Combining Mo-Cu/HZSM-5 with a two-stage catalytic pyrolysis system for pine sawdust thermal conversion

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Abstract

Mo-Cu/HZSM-5 catalysts for pine sawdust thermal conversion have been prepared by an impregnation method. The Mo-Cu/HZSM-5 catalysts and HZSM-5 were characterized by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD) and transmission electron microscopy (TEM). All characterization results indicated that the introduction of CuO is beneficial to the dispersion of MoO₃ in the HZSM-5. Combined with the two-stage catalytic pyrolysis system, the Mo-Cu/HZSM-5 catalysts were used for pine sawdust thermal conversion. The products included gas, bio-oil and bio-char. The gas was analyzed by Gas chromatography (GC). Gas chromatography-mass spectrometry (GC-MS) was used to identify the compounds in bio-oils. The water content, higher heating value (HHV) and viscosity of bio-oils were measured. The

HHV and elements of bio-char were determined. The results indicated that Mo(3%)-Cu(3%)/HZSM-5 treatment yielded the highest amount of C₆-C₁₂ hydrocarbons, showed a robust ability to convert methane in the gas to bio-oil, and displayed no significant difference in the properties of bio-char when compared to different treatments in the same pyrolysis conditions.

Keywords: Pine Sawdust; Mo-Cu/HZSM-5; Catalytic pyrolysis; Biofuel

1. Introduction

As a result of concerning global climate change, increasing transportation fuel demand and fossil energy reserve depletion, people are exploring more environmentally friendly solutions to satisfy the current energy consumption. [1] Biomass is considered to be one of the most promising alternatives to conventional fuels, since use of biomass for fuels can contribute the reduction of atmospheric CO₂ emissions, in addition to its low content of sulfur, nitrogen, and ash contents. [2] Biomass is the only renewable source of fixed carbon, which can be converted to liquid, solid and gaseous fuels. [3] Developing fuels from biomass is becoming an attractive option. [4]

Currently, there are several pyrolysis technologies being studied to convert solid biomass to bio-oil, such as fluidized beds [5, 6], spouted beds [7, 8], fixed beds [9, 10], vacuum reactors [11, 12].

These pyrolysis technologies conducted thermal decomposition processes in the absence of oxygen, in which biomass was heated to produce bio-oil or/and bio-char. [13] However, bio-oil cannot be used directly as transportation fuel, as it has negative properties such as high acidity, water content, viscosity, and instability. [14] Therefore, The challenge is to produce high quality bio-oil that can replace or supplement the current usage from traditional sources. [15] Two major routes, hydrodeoxygenation and catalytic cracking, were utilized to upgrade bio-oil to a hydrocarbon fuel. [16, 17] However, these routes from biomass to high quality fuel involve

multiple steps, thus greatly increasing the cost of biomass conversion. [18] Catalytic pyrolysis is an emerging technique used to produce hydrocarbon fuels directly from biomass, with the integration of catalysts during the pyrolysis. The high catalyst/biomass ratios ($\geq 1:1$) limits the application of this technique. [15, 19] A two-stage catalytic pyrolysis route is a pyrolysis process followed by a catalytic process, which not only decreases the catalyst/biomass ratio, but also eliminates energy consumption for re-heating and re-gasifying of raw bio-oil during upgrading processes.

Mo-Cu/HZSM-5 is a good catalyst for methane aromatization. [20] The support, HZSM-5, has robust catalytic cracking abilities. [21] Combining the two-stage catalytic pyrolysis system, it is beneficial to drive more carbon to bio-oil over Mo-Cu/HZSM-5, as gas from the pyrolysis process includes methane. However, there is no report of Mo-Cu/HZSM-5 for directly upgrading bio-oil vapor in catalytic pyrolysis process in literature. In this work, a series of Mo-Cu/HZSM-5 catalysts were prepared by the impregnation method. A two-stage catalytic pyrolysis system was developed. Mo-Cu/HZSM-5 catalysts were investigated for pine sawdust thermal conversion to hydrocarbon biofuels using the two-stage catalytic pyrolysis system. The aim was to determine the Mo-Cu/HZSM-5 mixture with the optimal Mo/Cu ratio to obtain better yield and quality of hydrocarbon biofuel based on the two-stage catalytic pyrolysis system.

2. Experimental

2.1. Preparation of Mo-Cu/HZSM-5 catalysts

Ammonia heptamolybdate (99 wt. %) and copper (II) nitrate (99 wt. %) were purchased from Aldrich (Milwaukee, WI) and used as received. The HZSM-5 molecular sieve with a Si/Al ratio of 30 was supplied by Zeolyst International (Conshohocken, PA). A series of Mo-Cu/HZSM-5

catalysts with different Cu/Mo molar ratios were prepared by a wet impregnation method. HZSM-5 powders were impregnated with aqueous solutions of a given amount of ammonia heptamolybdate and copper (II) nitrate, then calcinated at 550 °C for 5 h. The 40-60 mesh particle catalysts were recovered by sieve. All Mo-Cu/ZSM-5 catalysts were based on 3 wt. % Mo content.

2.2. Catalysts characterizations

2.2.1. BET

The BET specific surface area and porosity texture of each sample was determined by nitrogen adsorption measurements at 77.2 K with an automatic Micromeritics ASAP 2020 apparatus. The samples were first degassed at 573 K for approximately 6 h, then studied with a static volumetric technique. The specific surface area of the catalysts was computed according to the Brunauer-Emmett-Teller (BET) method, and the total pore volume was determined at a relative pressure $P/P_0=0.995$. Density functional theory (DFT) was used to characterize the pore size distribution.

2.2.2. XRD

XRD was used for phase identification and determination of the relative crystallinity. XRD measurements were carried out using Cu K α radiation on a RIGAKU SMARTLAB. The X-ray tube was operated at 40 kV and 44 mA, and the X-ray pattern was scanned with a step size of crystallites of 0.02° (2 θ) from 5 to 50° (2 θ) and a counting time of 1 s per step.

2.2.3. TEM

TEM was performed on a JEM 2100 with an accelerating voltage of 300 kV. Droplets of an ultrasonically dispersed suspension of each sample in ethanol were placed on a copper grid with

lacey carbon film and dried at ambient conditions for TEM characterizations. In order to obtain particle size distribution of copper, around 200 copper particles were identified and measured.

2.3. Product and feedstock characterization

The moisture content of the pine sawdust on a dry basis was determined by oven-drying method. [22] Elemental analysis was conducted to determine the C, H, N and O contents of pine sawdust using a CE-440 elemental analyzer. The viscosity analyzer (REOLOGICA Instruments AB Company Dynamic Viscosity) was used to measure dynamic viscosity at 20 °C. The HHV of samples was determined by a bomb calorimeter (Parr Instrument Company 1341). The moisture contents of bio-oil were measured by the Karl Fischer Titrator V20 (Mettler Toledo Company). Gas analysis was carried out on a GC (Agilent GC-7890A (Hp-5 column: 30 m × 0.25 mm × 0.25 µm)) with a combined TCD and FID. Standard gas mixtures were used for calibration, and argon was used as the carrier gas. GC-MS (Agilent GC-7890A (DB-5 column: 30 m × 0.25 mm × 0.25 µm)) and MSD-5975C (Electron ionization at 70 eV, mass range of 50–5000 m/z, semi-quantitation based on TIC, mass chromatograms)) was used to analyze the chemical composition of samples. The gas chromatograph was programmed at 60 °C for 1 min, followed by ramp 1 at 3 °C/min to 260 °C and ramp 2 at 5 °C/min to 280 °C. The temperature was held for an additional 10 minutes after each ramp. The injector temperature was 300 °C, and the injection size was 1 µL. The flow rate of the carrier gas (hydrogen) was 1 mL/min. The compositions were identified based on the NIST Mass Spectral Library and literature values. [23-25]

2.4. Experimental apparatus and procedure

The catalytic pyrolysis system was a novel coupled reactor configuration which includes a pyrolysis fixed-bed reactor, a catalytic fixed-bed reactor and a condenser system. The diameter

and the length of the pyrolysis reactor was 5.08 cm and 45.72 cm. The diameter and the length of the catalytic reactor was 2.54 cm and 40.64 cm. Both of the reactors consisted of a temperature controlled furnace and a fixed bed tube. Reaction products traveled through a condenser which was kept at -10 ± 2 °C. The final product included uncondensed gas, bio-oil and bio-char in the pyrolysis reactor. The schematic diagram of the two-stage catalytic pyrolysis system is shown in Fig. 1.

In each test, 100 g of pine sawdust was added into the pyrolysis reactor, then 10 g of Mo-Cu/HZSM-5 series catalyst was loaded. The treatments of no catalyst, HZSM-5, Mo(3%)/HZSM-5, Mo(3%)-Cu(6%)/HZSM-5, Mo(3%)-Cu(3%)/HZSM-5, Mo(3%)-Cu(1.5%)/HZSM-5 and Cu(3%)/HZSM-5 were represented by NC, 0-0, 3-0, 3-6, 3-3, 3-1.5 and 0-3, respectively. Nitrogen was used to remove the air in the system with 10 mL/min flow rate for 30 min. The catalytic reactor was heated at a rate of 30 °C/min to 500 °C. Then, the pyrolysis reactor was heated at a rate of 40 °C/min to 550 °C. The nitrogen flow rate was set at 3 mL/min. After 5 more minutes, the gas product samples were collected for GC analysis. The pyrolysis reactor at 550 °C and catalytic reactor at 500 °C was kept for 1 hour, After each test, the system was allowed to cool for 2 hours. The biofuel was collected from the condenser. Bio-char was collected by disassembling the pyrolysis reactor. The gas yield was calculated by subtracting the bio-char and bio-oil weights from the original feedstock weight.

In order to obtain the objective experiment results, each test was performed in duplicate. All observations were recorded in triplicate and average values were reported. All data was rounded to two decimals.

3. Results and discussion

3.1. Feedstock properties

Moisture content, HHV analysis and elemental analysis of the pine sawdust are presented in Table 1. Moisture content in biomass influences the heat transfer during the pyrolysis processes. [26] Generally, fast pyrolysis requires a dry feed ($\leq 10\%$ moisture). [27] The pine sawdust used had a moisture content of 6.6% which was fairly suitable for this study. The HHV of the pine sawdust (16.32 MJ/kg) is similar to that of other biomass such as corn stover, switch grass and prairie grass. The carbon content was 47.38%. Amounts of researchers have developed various techniques to convert carbon in biomass to final biofuels. [10] The reactivity and combustion behavior of biomass are strongly affected by its particle size. [28] The smaller particle sizes of the biomass benefit from a high heating transfer rate, which contributes to high-quality bio-oil. A scope of mono-layer pine sawdust particles was selected randomly. The 1004 particles were counted with the aid of the software (Nano-measurer 1.2) and the particle size distribution of sawdust was achieved. The mean particle size is 0.06 mm (Fig. 2).

3.2. Catalysts characterization

The XRD patterns of fresh catalysts were showed Fig. 3. The similarity of the XRD patterns between the parent HZSM-5 and the modified zeolite indicates that the framework of HZSM-5 was still retained after loading Cu and Mo. However, the HZSM-5 peak intensities differ depending on the Mo/Cu ratio. High intensities were observed for the catalyst HZSM-5, Mo(3%)/HZSM-5 and Cu(3%)/HZSM-5. The intensities for Mo(3%)-Cu(6%)/HZSM-5, Mo(3%)-Cu(3%)/HZSM-5 and Mo(3%)-Cu(1.5%)/HZSM-5 decreased significantly. With the increase of Mo/Cu ratio, the intensities of the peaks at 7.9° , 8.8° gradually decreased, and no MoO_3 or CuO phases could be detected for Mo(3%)-Cu(6%)/HZSM-5, Mo(3%)-Cu(3%)/HZSM-5 or Mo(3%)-Cu(1.5%)/HZSM-5. From the tests, it was obvious MoO_3 could

not be detected after the introduction of Cu. All XRD results indicated that the introduction of Cu was beneficial to the dispersion for Mo species, and an interaction between Cu and Mo along with HZSM-5 may be present in Mo-Cu/HZSM-5. [29]

Fig. 4 shows the bright field high resolution TEM images of catalysts. As seen in Fig. 4.a, there was no any dark spots because of no metal loading. Many dark spots were shown in Fig. 4.b and Fig. 4.c, which was attributed to the presence of metals oxide aggregates. The images in Fig. 4.c, Fig. 4.d, and Fig. 4.e also did not show any dark spots, indicating that MoO_3 and CuO were well-dispersed over the HZSM-5. All these results indicated that the introduction of CuO is beneficial to MoO_3 dispersion, which is consistent with the XRD characterization results.

As can be seen in Table 2, the BET surface area, Langmuir surface area and total pore volume decrease after the introduction of metals in HZSM-5. This made a textural alteration to the parent zeolite, possibly because of pore blocking by metal species dispersed in the channels, or by the presence of metal oxide aggregates. [30] DFT model simulation results (Fig. 5) indicated that the HZSM-5 and Mo-Cu/HZSM-5 series catalysts contain pores with a distribution of sizes between 1 and 20 nm.

3.3. Products yield

The mass balance obtained for the two-stage catalytic pyrolysis experiments is shown in Table 3. The data in Table 3 indicates that the bio-char yield was consistent and comparable due to the invariable pyrolysis conditions for the first fixed bed reactor. The bio-oils obtained in this research included two phases-aqueous phase and oil phase. The oil phase in bio-oil contained many organic chemicals. Compare to the no catalyst treatment, catalytic treatments reduced the yields of oil phase and increased the yields of aqueous phase. This was due to deoxygenation

reactions over HZSM-5 and Mo-Cu/HZSM-5 catalysts, which produced water. Among the catalytic treatments, the less introduction of Cu into Mo/HZSM-5 catalyst benefited improving the yield of oil phase. The second highest yield of oil phase were obtained by Mo(3%)-Cu(1.5%)/HZSM-5 treatment. Table 3 shows that the use of the catalyst reduced the yield of oil phase while increasing the gas yield. This was caused by the catalyst promoting secondary deoxygenation reactions of pyrolytic vapors, such as decarbonylation and decarboxylation. [31] For the reason that the temperature in the pyrolysis stage were the same in different treatment, the yields of bio-char from different treatments displayed no significant difference. After catalytic treatments the coking was found in the catalytic reactor. Although the yield of coking was not high, coking can deactivate catalyst remarkably. The specific analysis of the bio-char, bio-oil and gas will later be further illustrated.

3.4. Bio-oil analysis

The bio-oil products included aqueous and oil phases. The aqueous phase was mainly composed of water. The oil phase mainly consisted of organic compounds. Table 4 shows the physical properties of liquid bio-oil products in different treatments. The resulting oil phase was a dark brown liquid with a smoky odor. The bio-oil of non-catalytic treatment had the highest oil phase mass of 24.04 g. The bio-oil of catalytic treatments achieved relatively low oil phase mass. This may be due to the cracking behavior of HZSM-5-base catalysts, resulting in a decreased liquid yield and increased gas yield. The heating value of bio-oil by non-catalytic treatment was 24.71 MJ/kg. The bio-oil by catalytic treatments got higher heating values than the bio-oil by non-catalytic treatment. The highest heating value of bio-oil by catalytic treatments was 29.78 MJ/kg (Mo(3%)/HZSM-5 treatment). It indicated that Mo-Cu/HZSM-5 catalytic treatments can improve the heating value of bio-oil in these experiments. The viscosity declined from $13.10 \times$

10⁻³ Pa·s for bio-oil by non-catalytic treatment to less than 8.38×10^{-3} Pa·s, which was mainly due to catalytic cracking of HZSM-5 and Mo-Cu/HZSM-5. [32, 33] This improved its chemical and vaporization characteristics and resulted in lower water content and lower molecular weight, which is consistent with the research of Shihadeh [34]. The water content significantly influences physical properties such as the heating value, viscosity, density, acidity, stability and homogeneity of the oil phase of bio-oil. [31] The water content of the oil phase was decreased from 9.40 wt. % in bio-oil by non-catalytic treatment to less than 8.10 wt. %. Decreasing presence of aldehydes and ketones (Table 5) slightly made this oil phase of bio-oil hydrophobic, which benefits in declining water content in the oil phase of bio-oil.[35, 36]

In order to evaluate the two-stage catalytic pyrolysis process, the chemical composition of the bio-oils was analyzed using a GC-MS. The chemical names, chemical formula and relative contents are listed in Table 5. The bio-oil was a complex mixture highly oxygenated organics such as esters, ethers, aldehydes, ketones, phenols, organic acids and alcohols. [37] These chemicals originated from the degradation of cellulose, hemicellulose and lignin in the pine sawdust. [24] The similar composition of bio-oil in different treatments implied similar transformation pathways of typical compounds to some extent.

The effect of the Mo-Cu/HZSM-5 catalysts (different Mo/Cu ratios) on bio-oil compositions was analyzed. From Table 5, the oil phase of bio-oil produced by non-catalytic treatment mainly included esters, phenols, alcohols, ketones and heavy hydrocarbons ($> C_{15}$). In contrast to the products obtained by non-catalyst, the content of esters decreased to some degree in the catalyzed product. Especially the Mo-Cu/HZSM-5 (Mo/Cu ratio of 1:1) treatment got lowest esters content 11.97%. Compared to the non-catalytic treatment, catalytic treatments increased the total proportion of phenols and especially increased the contents of light phenols, such as

phenol and 3-methyl-phenol. This is possibly caused by the Mo-Cu/HZSM-5 converting heavy phenols to light phenols through cracking, decarbonylation and demethoxylation. [31, 38] The bio-oil obtained by HZSM-5 catalyst treatment contained less phenols than the bio-oil by Mo-Cu/HZSM-5 treatments, which indicates that loading Mo and Cu to HZSM-5 benefits in improving the cracking performance. The aldehydes can be declined (0-0, 3-0) or even eliminated (3-6, 3-3, 3-1.5 and 0-3). This may be due to a series of transformations of acetalization, etherification and rearrangement, or by thermal degradation into carbonaceous deposits. [39] Ethers were also eliminated when exposed to HZMS-5 and Mo-Cu/HZSM-5 in this experimental system. Secondary degradation reactions by the catalysts helped in decreasing the ketone content in the oil phase of bio-oil. The Mo (3%)/HZSM-5 catalyst performed well when converting ketones compared to all the Mo-Cu/HZSM-5 series catalysts. It seems that Mo-Cu/HZSM-5 series catalyst had good performance on decreasing ketones content in the bio-oil.

The hydrocarbons in the bio-oil are the most important components researchers have focused on. The strong Brønsted acid sites in the support HZSM-5 promote the production of aromatics through dehydration, cracking, decarbonylation, decarboxylation and aromatization. [13] A closer inspection of Table 5 appears to suggest that the production of hydrocarbons increased for all catalytic treatments, with HZSM-5 having the most effect. The hydrocarbons in the oil phase of the bio-oil obtained by HZSM-5 treatment were heavy compounds ($> C_{15}$) such as decahydro-4a-methyl-1-methylene-7-(1-methylethylidene)-(4aR-trans)-Naphthalene, 1-methyl-7-(1-methylethyl)-Phenanthrene and 6-ethyl-1,2,3,4-tetrahydro-1,1,4,4-tetramethyl-7-(1-methylethenyl)-Naphthalene. Both Mo(3%)/HZSM-5 treatment and Mo(3%)-Cu(3%)/HZSM-5 treatment appear to increase the production of C_6 - C_{12} hydrocarbons in the oil phase of bio-oil.

When the MoO_3 or/and CuO was introduced into Mo/HZSM-5, Cu/HZSM-5 and Mo-Cu/HZSM-

5 catalysts, the framework of HZSM-5 interacted with MoO₃ and CuO at channels which decreased the Brønsted acid sites, which may result in obtaining more light hydrocarbon.

Besides, Mo-Cu/HZSM-5 is an efficient catalyst on methane aromatization. [20] Methane was one of components in the vapor from the pyrolysis reactor. The XRD and TEM characterization indicated that an interaction between Cu and Mo along with HZSM-5 existed in Mo-Cu/HZSM-5. This interaction probably result in a favorable structure for methane aromatization reactions over Mo-Cu/HZSM-5 catalysts. Therefore, CH₄ can be converted to an aromatic hydrocarbon over Mo-Cu/HZSM-5 catalysts.

3.5. Gas analysis

The gaseous products contained N₂, H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, C₄H₈ and C₄H₁₀. Their content are displayed in the Table 6. During bio-oil upgrading process, CO could be produced by decarbonylation reactions in the presence of HZSM-5-base catalysts. [40] The preferable method of oxygen removal is to form CO₂ during upgrading reactions. [41] Gas composition varied with different treatments. The main components of gas were CO₂ and CO, although their contents changed marginally. The contents of CO₂ were around 42%. The contents of CO were around 31%. The contents of C₂₋₅ changed slightly. Whereas CH₄ contents changed in a special way. The Mo(3%)-Cu(3%)/HZSM-5 treatment and Mo(3%)-Cu(1.5%)/HZSM-5 treatment could get low CH₄ contents. It might be due to the Mo (3%)-Cu (3%)/HZSM-5 and Mo (3%)-Cu(1.5%)/HZSM-5's ability of efficient methane aromatization.

3.6. Bio-char analysis

Bio-char is a solid material obtained from the carbonization of biomass. [42] The physical properties of bio-char are also depicted in Table 6. All treatments in the pyrolysis reactor were

conducted under the same conditions. The HHV and carbon content of bio-char have no big difference.

4. Conclusion

In this work, Mo-Cu/HZSM-5 catalysts with different Mo/Cu ratios were developed by the impregnation method. The characterization results from BET, XRD and TEM indicated that the introduction of CuO is beneficial to the dispersion of MoO₃ in the HZSM-5. The Mo-Cu/HZSM-5 catalysts were used for pine sawdust thermal conversion in the two-stage catalytic pyrolysis system. Based on the analysis of gas and bio-oil, the results indicated that Mo(3%)-Cu(3%)/HZSM-5 catalyst yielded the highest amount of C₆-C₁₂ hydrocarbons, displayed a robust ability to convert methane in the gas to the bio-oil. All treatments including no catalyst treatment HZSM-5 treatment and Mo-Cu/HZSM-5 with different Mo/Cu ratios treatments displayed no significant difference in the properties and yields of bio-char.

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Figure captions:

Fig. 1.

The schematic diagram of the two-stage catalytic pyrolysis system.

Fig. 2.

Particle size distribution of the pine sawdust.

Fig. 3.

XRD patterns of catalysts (a) HZSM-5, (b) Mo(3%)/HZSM-5, (c) Mo(3%)-Cu(6%)/HZSM-5, (d)
Mo(3%)-Cu(3%)/HZSM-5, (e) Mo(3%)-Cu(1.5%)/HZSM-5 and (f) Cu(3%)/HZSM-5.

Fig. 4.

TEM images of HZSM-5 (a), Mo(3%)/HZSM-5 (b), Mo(3%)-Cu(6%)/HZSM-5 (c), Mo(3%)-
Cu(3%)/HZSM-5 (d), Mo(3%)-Cu(1.5%)/HZSM-5 (e) and Cu(3%)/HZSM-5 (f) catalysts.

Fig. 5.

Pore size distribution of HZSM-5 and Mo-Cu/HZSM-5 series catalysts.

Fig. 6.

The product distribution of the bio-char, bio-oil and gas.

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Fig. 1.The schematic diagram of the two-stage catalytic pyrolysis system.

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Fig. 2. Particle size distribution of the pine sawdust.

Fig. 3. XRD patterns of catalysts (a) HZSM-5, (b) Mo(3%)/HZSM-5, (c) Mo(3%)-Cu(6%)/HZSM-5, (d) Mo(3%)-Cu(3%)/HZSM-5, (e) Mo(3%)-Cu(1.5%)/HZSM-5 and (f) Cu(3%)/HZSM-5.

Fig. 4. TEM images of HZSM-5 (a), Mo(3%)/HZSM-5 (b), Mo(3%)-Cu(6%)/HZSM-5 (c), Mo(3%)-Cu(3%)/HZSM-5 (d), Mo(3%)-Cu(1.5%)/HZSM-5 (e) and Cu(3%)/HZSM-5 (f) catalysts.

Fig. 5. Pore size distribution of HZSM-5 and Mo-Cu/HZSM-5 series catalysts.

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Table 1 Characterizations of the pine sawdust

Analysis	Data
Moisture Content (wt. %)	6.60
Elements Analysis (wt. %)	Carbon 47.38
	Hydrogen 6.42
	Nitrogen 0.99
	Oxygen 44.96
HHV (MJ/kg)	16.32

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Table 2 BET parameters of the various samples.

Sample	BET Surface area (m ² /g)	Langmuir Surface area (m ² /g)	Total Pore volume (cm ³ /g)
HZSM-5	432.18	517.44	0.37
Mo(3%)/HZSM-5	364.33	433.84	0.32
Mo(3%)-Cu(6%)/HZSM-5	122.77	157.51	0.24
Mo(3%)-Cu(3%)/HZSM-5	166.45	229.64	0.28
Mo(3%)-Cu(1.5%)/HZSM-5	206.45	263.38	0.29
Cu(3%)/HZSM-5	372.87	426.06	0.35

Table 3 The product distribution of gas, solid and liquid.

Treatments	Gas	Solid		Liquid	
		Bio-char	Coking	Aqueous phase	Oil phase
NC	22.71	24.40	0.00	28.85	24.04
0-0	29.99	23.98	0.47	31.89	13.67
3-0	25.38	22.95	0.72	38.21	12.74
3-6	28.13	24.98	0.68	35.12	11.09
3-3	28.74	25.15	0.49	32.06	13.56
3-1.5	26.68	23.88	0.52	32.31	16.61
0-3	29.37	23.74	0.39	33.48	13.02

Table 4 The properties of bio-oils.

Treatments	Higher heating value		Viscosity		Water content	
	MJ/kg		10^{-3} Pa·s		wt. %	
	AP	OP	AP	OP	AP	OP
NC	-	24.71	6.23	13.1	84.30	9.40
0-0	-	28.50	6.23	13.1	87.20	8.10
3-0	-	29.78	6.22	7.48	87.70	6.90
3-6	-	24.87	6.29	7.42	90.30	4.50
3-3	-	29.23	6.22	3.49	91.20	4.30
3-1.5	-	26.57	6.24	6.49	89.80	6.50
0-3	-	25.35	6.25	8.38	87.60	7.40

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551 **Table 5** Chemical composition of the oil phases in bio-oils.

Compounds		Relative content (%)						
		NC	0-0	3-0	3-6	3-3	3-1.5	0-3
Acids						1.77		
Benzoic acid, 2,5-dimethyl-	C ₉ H ₁₂ O ₂					1.77		
Esters		20.48	17.14	17.83	16.56	11.97	19.11	16.82
Methyl 3-butyrate	C ₅ H ₆ O ₂						0.99	0.63
2-Butyric acid, di-2-propenyl ester	C ₁₀ H ₁₀ O ₄						1.15	
2,6-Naphthalenedicarboxylic acid, dimethyl ester	C ₁₄ H ₁₂ O ₄	3.00						
Fumaric acid, dec-4-enyl propyl ester	C ₁₇ H ₂₈ O ₄	0.92						
8,11-Octadecadienoic acid, methyl ester	C ₁₉ H ₃₀ O ₂		0.51					
9-Octadecenoic acid, methyl ester, (E)-	C ₁₉ H ₃₆ O ₂				0.68			
7-Oxodehydroabietic acid, methyl ester	C ₂₁ H ₂₈ O ₃			0.97		2.22		
1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester, [1R-(1.alpha.,4a.beta.,10a.alpha.)]-	C ₂₁ H ₃₀ O ₂	16.56	16.63	16.41	15.88	9.75	16.97	16.19
Phenols		29.65	24.23	36.22	40.75	37.91	38.00	40.43
Phenol	C ₆ H ₆ O	1.65	3.41	4.76	5.97	4.13	3.57	3.28
Phenol, 2-methyl-	C ₇ H ₈ O				3.57			
Phenol, 3-methyl-	C ₇ H ₈ O	0.53	3.37	1.60		1.73	2.50	4.19
Phenol, 2-methoxy-	C ₇ H ₈ O ₂	14.30	5.13	15.91	12.07	12.00	11.14	11.78
Phenol, 2,6-dimethyl-	C ₈ H ₁₀ O				0.68		0.56	
Phenol, 2-methoxy-4-methyl-	C ₈ H ₁₀ O ₂	7.15	8.40	10.93	10.71	12.66	10.00	7.91
2-Methoxy-4-vinylphenol	C ₉ H ₁₀ O ₂	1.66	3.92		1.34		2.89	0.80
Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂	4.36		3.02	3.01	7.39	2.44	6.80
Phenol, 2-methoxy-4-(1-propenyl)-	C ₁₀ H ₁₂ O ₂				3.40		2.71	5.17
Phenol, 2-methoxy-4-propyl-	C ₁₀ H ₁₄ O ₂							0.50
Phenol, 4-(3,4-dihydro-2,2,4-trimethyl-2H-1-benzopyran-4-yl)-	C ₁₈ H ₂₀ O ₂						2.19	
Aldehydes		1.51			1.76	0.50	2.41	0.84
2-Furancarboxaldehyde, 5-methyl-	C ₆ H ₆ O ₂	1.51			1.76	0.50	2.41	
Benzaldehyde, 2-(2-propynyloxy)-	C ₁₀ H ₈ O ₂							0.84
Alcohols		9.01	4.85	1.35	0.79	0.48		
Benzenemethanol, 4-methyl-	C ₈ H ₁₀ O					0.48		
2,3-Dimethoxybenzyl alcohol	C ₉ H ₁₂ O ₃	1.62						
Eugenol	C ₁₀ H ₁₂ O ₂	3.93	2.22	1.35				
Verrucarol	C ₁₅ H ₂₂ O ₄	3.46						
3,6-Dimethoxy-4-phenanthrol	C ₁₆ H ₁₄ O ₃		2.63		0.79			
Ketones		18.83	3.72	3.27	5.09	8.10	5.09	4.82
1,2-Cyclopentanedione, 3-methyl-	C ₆ H ₈ O ₂				0.83		0.66	
2-Cyclopenten-1-one, 2-methyl-	C ₆ H ₈ O	1.07	0.62	0.63	0.53	0.45	0.75	0.55
2-Methyl-2,3-divinylloxirane	C ₇ H ₁₀ O	0.73						
Ethanone, 1-(3-methylphenyl)-	C ₉ H ₁₀ O				0.56		0.58	
Alantolactone, 4.alpha.,4A.alpha.-epoxy-	C ₁₅ H ₂₀ O ₃						0.65	
Anthracene, 1,4-dimethoxy-	C ₁₆ H ₁₄ O ₂	1.97	3.10	2.64		1.68		3.43
Anthracene, 9,10-dimethoxy-	C ₁₆ H ₁₄ O ₂				3.17		2.45	
2,6-Di(2-furylmethylidene)cyclohexan-1-one	C ₁₆ H ₁₄ O ₃	3.94						
Phenanthrene, 3,6-dimethoxy-9-methyl-	C ₁₇ H ₁₆ O ₂							0.84
2-Acetyl-9,10-dimethylanthracene	C ₁₈ H ₁₆ O					0.99		
1,7,7-Trimethyl-3-phenethylidenebicyclo[2.2.1]heptan-2-one	C ₁₈ H ₂₂ O	1.20						
Spiro[cyclobutane-1,1'(2'H)-phenanthren]-2-one, 3',4',4'a,9',10',10'a-hexahydro-4'a-methyl-, (1'.alpha.,4'a.beta.,10'a.alpha.)-	C ₁₈ H ₂₂ O	0.93				1.03		

Ethanone, 1-(1,2,3,5,6,7-hexahydro-1,1,5,5-tetramethyl-s-indacen-4-yl)-	C ₁₈ H ₂₄ O	6.36						
s-Indacen-1(2H)-one, 3,5,6,7-tetrahydro-3,3,4,5,5,8-hexamethyl-	C ₁₈ H ₂₄ O					3.95		
(3E,5E,7E)-6-Methyl-8-(2,6,6-trimethyl-1-cyclohexenyl)-3,5,7-octatrien-2-one	C ₁₈ H ₂₆ O	2.63						
Ethers		1.20						
(4-Methoxymethoxy-hex-5-ynylidene)-cyclohexane	C ₁₂ H ₂₂ O ₂	1.20						
4-Acetylphenyl ether	C ₁₆ H ₁₄ O ₃				1.44			
Hydrocarbons		13.19	41.76	34.07	25.71	36.51	30.11	27.75
3-Hexyne	C ₆ H ₁₀		0.57	0.52		0.64		
5-Methyl-3-heptene	C ₈ H ₁₆					0.79		
6-Methyl-3-heptyne	C ₈ H ₁₄					0.96		
Indene	C ₉ H ₈	1.10	0.67			0.76		1.05
Indane	C ₉ H ₁₀		0.58					
Benzene, 1-ethyl-2-methyl-	C ₉ H ₁₂		0.56			0.69		
1,3,5-Cycloheptatriene, 7-ethyl-	C ₉ H ₁₂		1.08			1.38		
Tricyclo[3.2.1.0(2,4)]octane, 3-methylene-	C ₉ H ₁₂	1.14						
Naphthalene	C ₁₀ H ₈	3.81	1.15	0.72		1.18		1.29
Naphthalene, 1,2-dihydro-	C ₁₀ H ₁₀	0.65				0.32		
1,4-Dihydronaphthalene	C ₁₀ H ₁₀		0.73			0.61		
1H-Indene, 1-methyl-	C ₁₀ H ₁₀				0.52			0.51
3-Phenylbut-1-ene	C ₁₀ H ₁₂							0.55
1H-Indene, 2,3-dihydro-2-methyl-	C ₁₀ H ₁₂	1.13						
Naphthalene, 2-methyl-	C ₁₁ H ₁₀	2.87	2.48	2.10		1.64		3.02
1,6-Ethenoazulene, 1,3a,6,8a-tetrahydro-	C ₁₂ H ₁₂					0.57		
Phenanthrene, 1-methyl-	C ₁₅ H ₁₂					0.45		
Phenanthrene, 4-methyl-	C ₁₅ H ₁₂			0.71			0.82	
1,2-Diphenylcyclopropane	C ₁₅ H ₁₄					0.55		
Naphthalene, decahydro-4a-methyl-1-methylene-7-(1-methylethylidene)-, (4aR-trans)-	C ₁₅ H ₂₄	1.45						
Phenanthrene, 3,6-dimethyl-	C ₁₆ H ₁₄				1.89	2.68	2.40	1.54
Phenanthrene, 2,7-dimethyl-	C ₁₆ H ₁₄			0.73				
Phenanthrene, 2,5-dimethyl-	C ₁₆ H ₁₄	0.96	0.83					
1,3,5-Cycloheptatriene, 6-methyl-1-(6-methyl-1,3,5-cycloheptatrien-1-yl)-	C ₁₆ H ₁₈		0.79					
Cyclopropane, 1,1-dimethyl-2-(2-phenyl-1-pentenylidene)-	C ₁₆ H ₂₀					0.83		
1,5,9-Decatriene, 1-phenyl-	C ₁₆ H ₂₀			0.68				
Phenanthrene, 2,3,5-trimethyl-	C ₁₇ H ₁₆	1.41	0.62		1.27	1.15	1.63	2.11
Phenanthrene, 1,2,3,4,4a,9,10,10a.alpha.-octahydro-1,1,4a.beta.-trimethyl-	C ₁₇ H ₂₄						0.82	
Phenanthrene, 1-methyl-7-(1-methylethyl)-	C ₁₈ H ₁₈	7.70	14.47	13.09	10.54	13.20	11.99	6.89
8-Isopropyl-1,3-dimethylphenanthrene	C ₁₉ H ₂₀		0.52	0.69				0.65
Naphthalene, 6-ethyl-1,2,3,4-tetrahydro-	C ₁₉ H ₂₂	2.98	2.12		2.84		3.63	
1,1,4,4-tetramethyl-7-(1-methylethenyl)-								
4b,8-Dimethyl-2-isopropylphenanthrene,	C ₁₉ H ₂₈		10.35	10.49	4.53	8.11	8.25	9.09
4b,5,6,7,8,8a,9,10-octahydro-								
Phenanthrene, 7-ethenyl-	C ₁₉ H ₂₈						0.57	
1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydro-								
4a,7-dimethyl-1-methylene-, [4aS-(4a.alpha.,4a.beta.,7.beta.,10a.beta.)]-								
Phenanthrene, 1,2,3,4,4a,9,10,10a-octahydro-	C ₂₀ H ₃₀				0.59			1.05
1,1,4a-trimethyl-								
Stigmastan-3,5-diene	C ₂₉ H ₄₈	0.10						

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Table 6 The analysis of gas and bio-char obtained by different treatments

		NC	0-0	3-0	3-6	3-3	3-1.5	0-3
Gas	N ₂ (volume %)	14.74	12.63	12.12	17.16	17.93	15.83	9.00
	H ₂ (Volume %)	3.01	2.10	2.13	2.94	2.68	2.91	2.67
	CO ₂ (Volume %)	41.52	43.73	42.65	40.51	41.98	43.87	43.22
	CO (Volume %)	32.01	30.86	32.19	33.11	31.02	30.45	31.57
	CH ₄ (Volume %)	6.58	5.18	3.99	1.81	0.13	0.11	5.84
	C ₂ H ₄ (Volume %)	0.54	1.79	1.68	1.15	1.76	1.72	2.04
	C ₂ H ₆ (Volume %)	0.75	1.98	2.91	1.59	1.84	2.49	1.38
	C ₃ H ₆ (Volume %)	0.40	0.72	1.22	0.94	1.92	1.42	2.97
	C ₃ H ₈ (Volume %)	0.26	0.59	0.65	0.49	0.13	0.63	0.43
	C ₄ H ₈ (Volume %)	0.06	0.30	0.33	0.19	0.48	0.44	0.60
	C ₄ H ₁₀ (Volume %)	0.13	0.12	0.13	0.11	0.13	0.13	0.08
Bio-char	HHV (MJ/kg)	29.20	29.09	29.16	28.89	29.13	28.95	29.11
	C (wt. %)	79.74	79.83	80.01	79.65	79.98	80.05	79.59
	H (wt. %)	1.39	1.36	1.28	1.33	1.27	1.35	1.28

Butene (C₄H₈) includes trans-2-butene, cis-2-butene and 1-butene.

Butane (C₄H₁₀) includes iso-butane, n-butane.